

CLAIMS:

1. Aprotic electrolytic composition for electrochemical generator, said generator including a separator and at least one composite electrode, said composite electrode containing a powder of inactive material for the electrode and, if necessary, an electronic conduction additive, said aprotic electrolytic composition being localized in the separator and in at least said composite electrode, characterized in that it comprises a first polymer matrix consisting of a polyether and at least one second polymer matrix, which are macroscopically separated, and in that it also comprises at least one alkali metal salt, as well as at least one polar aprotic solvent, said matrices being swellable by at least one said polar aprotic solvent, said solvent or mixture of solvents being unequally distributed between the matrices.
2. Electrolytic composition according to claim 1 characterized in that the macroscopic separation of the polymer matrices is localized at the interface between the composite electrode and the separator.
3. Electrolytic composition according to claim 1 characterized in that the macroscopic separation of the polymer matrices is localized inside the composite electrode.
4. Electrolytic composition according to claim 1 characterized in that the macroscopic separation of the polymer matrices is localized inside of the separator.
5. Electrolytic composition according to claim 1 characterized in that the first polymer matrix is comprised within the separator.
6. Electrolytic composition according to claim 1 characterized in that the distribution of the aprotic solvent between the polymer matrices is obtained by controlling the rate of cross-linking of each matrix.
7. Electrolytic composition according to claim 1 characterized in that the distribution of the aprotic solvent between the polymer matrices is obtained by introducing a solid filler in at least one of the polymer matrices.

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8. Electrolytic composition according to claim 1 characterized in that the distribution of the aprotic solvent between the polymer matrices is obtained by a choice of solvent and its different affinity for the different polymer matrices.

9. Electrolytic composition according to claim 1 characterized in that the distribution of the aprotic solvent between the polymer matrices is obtained by choosing the polymers.

10. Electrolytic composition according to claim 1 characterized in that at least one of the matrices is only slightly swollen by the aprotic solvent.

11. Electrolytic composition according to claim 1 characterized in that the polyether matrix in the separator has a swelling rate lower than that of the polymer matrix which is present in at least one composite electrode.

12. Electrolytic composition according to claim 1 characterized in that one of the polymer matrices which is present in at least one composite electrode is only slightly swollen, the porosity of said composite electrode being compensated by said polar aprotic solvent.

13. Electrolytic composition according to claim 1 characterized in that the first polyether matrix consists of a mixture of cross-linkable polyether and at least another polyether or polyether based oligomer including polyfunctional cross-linkable chemical groups enabling to give an interpenetrated network.

14. Electrolytic composition according to claim 1 characterized in that the first matrix consists of a mixture of a non cross-linkable polyether and at least another polyether or polyether based oligomer including polyfunctional cross-linkable chemical groups enabling to obtain a semi-interpenetrated network.

15. Electrolytic composition according to claim 1 characterized in that the first polymer matrix consists of a mixture of cross-linkable polyether and at least one cross-linking additive.

16. Electrolytic composition according to claim 15 characterized in that the cross-linking additive is selected from trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, polyethylene oxide diacrylate, polyethylene

oxide dimethacrylate, glycerol triacrylate, glycerol trimethacrylate, pentaerythiol tetraacrylate, glycerol propoxylate (1PO/OH) triacrylate, dipentaerythiol penta/hexaacrylate and di (watriethylolpropane) tetraacrylate.

17. Electrolytic composition according to claim 1 characterized in that it is obtained by cross-linking one of the two polymer matrices in the presence of the other polymer matrix.

18. Electrolytic composition according to claim 1 characterized in that the quality of the interface and the adhesion between the polymer matrices is maintained and/or improved by adding at least one polymer, oligomer, or monomer including multidimensional cross-linkable chemical groups enabling to obtain an interpenetrated network in physical contact with the two matrices.

19. Electrolytic composition according to claim 1 characterized in that the quality of the interface and the adhesion between the polymer matrices is maintained and/or improved by adding at least one polymer or non cross-linkable oligomer in physical contact with the matrices and capable of interacting by means of polar groups with each of the polymer matrices of the electrolytic composition.

20. Electrolytic composition according to claim 1 characterized in that at least one fraction of the anionic groups of an alkali metal salt are fixed on at least one of the polymer matrices.

21. Electrolytic composition according to claim 1 characterized in that the first polymer matrix consists of a non cross-linkable and swellable polyether.

22. Electrolytic composition according to claim 1 characterized in that the first polyether matrix consists of a cross-linkable polyether which is used to limit the rate of swelling.

23. Electrolytic composition according to claim 1 characterized in that the second polymer matrix is selected from vinylidene-*co*-hexafluoropropene, vinylidene fluoride, (PVDF), polyacrylonitrile, (PAN), methyl polymethacrylate, (PMMA), poly(ethylene propylene diene), (EPDM), and a polyether, the latter being selected so as to absorb an amount of aprotic which is different from that of the first polymer matrix.

24. Compound according to claim 1 characterized in that the polar aprotic solvent(s) are selected from propylene carbonates, ethylene carbonate, tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxolane, 4,4-dimethyl-1,3-dioxolane, γ -butyrolactone, butylene carbonate, sulfolane, 3-methylsulfolane, tert-butyl-ether, 1,2-dimethoxyethane, 1,2-diethoxyethane, bis(methoxyethyl)ether, 1,2-ethoxymethoxyethane, tetrbutylmethylether, glymes and sulfamides of formula:: $R_1R_2N-SO_2-NR_3R_4$, in which R_1 , R_2 , R_3 and R_4 are alkyl groups comprising between 1 and 6 carbon atoms and/or oxyalkyl groups comprising between 1 and 6 carbon atoms.

25. Electrolytic composition according to claim 1 characterized in that at least one of the polymer matrices is used to partially or totally coat the material of the positive electrode.

26. Electrolytic composition according to claim 1 characterized in that at least one of the polymer matrices is used to partly or completely coat the material of the negative electrode.

27. Electrochemical generator comprising a negative electrode and a positive electrode, said electrodes being reversible to alkali ions, as well as a polymer electrolyte separator, characterized in that the electrolytic component of the generator is a composition according to one of claims 1 to 26.

28. Electrochemical generator according to claim 27 characterized in that the polymer matrix in contact with the material of the positive electrode is electrochemically stable in the presence of said material of the positive electrode.

29. Electrochemical generator according to claim 27 characterized in that the polymer matrix in contact with the negative electrode is electrochemically compatible with the material of the negative electrode.

30. Electrochemical generator according to claim 27 in which the electrolytic component comprises at least one lithium salt.

31. Electrochemical generator according to claim 27 in which the negative electrode consists of metallic lithium.

32. Electrochemical generator according to claim 27 in which the two electrodes are composite electrodes utilizing insertion materials which are reversible to lithium.

33. Electrochemical generator according to claim 27 in which the negative electrode is a carbon composite.

34. Electrochemical generator according to claim 27 in which the negative electrode is a carbon composite in which the binder is a polyether based polymer matrix.

35. A two-step process for manufacturing a sub-assembly of an electrochemical generator according to claim 27, including a porous composite electrode and a separator in whole or in part:

the first step consisting in coating under air an electrode support with a mixture containing an electrode material, a polymer and a coating solvent, if necessary, said polymer constituting the second polymer matrix of the electrolytic composition as defined in one of claims 1 to 26, said second polymer matrix being slightly swellable by one or more polar aprotic solvents, and acting as a binder of the electrode material, thereby obtaining a porous composite electrode;

the second step consisting in overspreading under anhydrous condition on the previously dried porous composite electrode obtained in the first step, a polyether based polymer or prepolymer constituting the first polymer matrix of the electrolytic composition as defined in one of claims 1 to 26, said first polymer matrix being cross-linkable thermally, by UV or electron beam (EB) radiation and chemically swellable by a polar aprotic solvent and, if needed, a volatile organic diluent, said liquid aprotic solution comprising at least one alkali metal salt, so as to compensate for the total or partial porosity of said electrode by said solution and to constitute at the surface of said electrode a coating so as to form the separator in whole or in part.

36. Two-step process of manufacturing a sub-assembly of an electrochemical generator according to claim 35 where the polymer constituting the second polymer matrix of said electrolytic composition is slightly swellable by one or more polar aprotic solvents and acts as binder, and is selected from vinylidene fluoride-*co*-hexafluoropropene, vinylidene fluoride, (PVDF), polyacrylonitrile,

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(PAN), methyl polymethacrylate, (PMMA), poly(ethylene propylene diene), (EPDM).

37. Three-step process of manufacturing a sub-assembly of an electrochemical generator according to claim 27, including a porous composite electrode, and a separator in whole or in part:

the first step consisting in coating under air with a mixture containing an electrode material, a polymer and a coating solvent, if necessary, said polymer constituting a second polymer matrix of the electrolytic composition as defined in one of claims 1 to 26, said second polymer matrix being slightly swellable with one or more polar aprotic solvents, and acting as binder of said electrode material, thereby obtaining a porous composite electrode;

the second step consisting in overspreading under anhydrous condition on a previously dried porous composite electrode, a liquid aprotic solution comprising a polymer or a polyether based prepolymer constituting a third polymer matrix of the electrolytic composition as defined in one of claims 1 to 26, said third matrix being cross-linkable thermally, by UV radiation or with an electron beam (EB) and being chemically swellable by a polar aprotic solvent and, if needed, a volatile organic diluent as well as at least one alkali metal salt, so as to compensate for the porosity of said electrode by said solution;

the third step consisting in overspreading under anhydrous condition on the composite electrode obtained in the second step a liquid aprotic solution comprising a polymer or a polyether based prepolymer constituting the first matrix of the electrolytic composition as defined in one of claims 1 to 26, said first matrix being cross-linkable thermally, by UV radiation or with an electron beam (EB) and chemically swellable by a polar aprotic solvent in which the swelling rate is lower than that of the polyether used to compensate for the porosity of the composite obtained in the second step and, if needed, a volatile organic diluent as well as at least one alkali metal salt, so as to constitute at the surface of said electrode a coating forming the separator in whole or in part.

38. Three-step process for manufacturing a sub-assembly of an electrochemical generator according to claim 37 where the polymer which constitutes the second polymer matrix of the electrolytic composition is slightly swellable by one or more polar aprotic solvents and acts as binder, and is selected from vinylidene fluoride-*co*-hexafluoropropene, vinylidene fluoride, (PVDF),

polyacrylonitrile, (PAN), methyl polymethacrylate, (PMMA), poly(ethylene propylene diene), (EPDM).

39. Two-step process for manufacturing a sub-assembly of an electrochemical generator according to claim 27, including a composite electrode and a separator in whole or in part:

the first step consisting in coating under anhydrous condition an electrode support with a mixture containing an electrode material, a polyether based polymer or prepolymer, at least one polar aprotic solvent, at least one alkali metal salt, and a coating solvent if necessary, said polyether based polymer constituting the second polymer matrix of the electrolytic composition such as defined in one of claims 1 to 26, said second matrix being cross-linkable thermally, by UV radiation or with an electron beam (EB) and being chemically swellable by a polar aprotic solvent;

the second step consisting in overspreading under anhydrous condition on the composite electrode obtained in the first step a liquid aprotic solution comprising a polyether based polymer or prepolymer constituting the first polymer matrix of the electrolytic composition such as defined in one of claims 1 to 26, said first matrix being cross-linkable thermally, by UV radiation or an electron beam (EB) and being chemically swellable by a polar aprotic solvent but in which the swelling rate is lower than that of the second polyether matrix used in the composite electrode and, if needed, a volatile organic diluent as well as at least one alkali metal salt, so as to constitute at the surface of said electrode a coating to form the separator in whole or in part.

40. Two-step process for manufacturing an anodic sub-assembly of an electrochemical generator according to claim 39, characterized in that the composite electrode is a carbon anode.

41. Two-step process for manufacturing an anodic sub-assembly of an electrochemical generator according to claim 37, characterized in that the composite electrode is a composite cathode in which the electrode material is a phosphate of a transition metal operating at 3.5 -3.7V.

42. Two-step process for manufacturing a sub-assembly of an electrochemical generator according to claim 27, including a porous composite electrode and a separator in whole or in part:

the first step consisting in coating under air an electrode support with a mixture containing an electrode material, a polymer and a coating solvent, if necessary, said polymer constituting the second polymer matrix of the electrolytic composition as defined in one of claims 1 to 26, said second polymer matrix being slightly swellable by one or more polar aprotic solvents, and acting as binder of the electrode material, thereby obtaining a porous composite electrode;

the second step consisting in overspreading under anhydrous condition on the previously dried porous electrode obtained in the first step a liquid aprotic solution comprising a polyether which is chemically swellable by one or more polar aprotic solvents, and a prepolymer, oligomer or monomer which is cross-linkable thermally, by UV radiation or with an electron beam (EB), the polyether and the prepolymer, oligomer or monomer forming the first polymer matrix of the electrolytic composition as defined in one of claims 1 to 26 and, if necessary, a volatile organic diluent as well as at least one alkali metal salt, so as to compensate for the porosity in whole or in part of said electrode by said solution and to constitute at the surface of said electrode a coating so as to form the separator in whole or in part.

43. Two-step process for manufacturing a sub-assembly according to claim 42, characterized in that the polyether used in said solution is cross-linkable thermally, by UV radiation or with an electron beam (EB).

44. Process of assembling an electrochemical generator according to claim 27, by joining by lamination or pressing two sub-assemblies, one anodic and one cathodic, manufactured according to claims 35, 36, 39 and 42.

45. Process of assembling an electrochemical generator according 27, by joining by lamination or pressing two sub-assemblies, one anodic and one cathodic, manufactured according to claims 35, 36 and 42, the porosity of one of the two sub-assemblies being only partially compensated, said porosity being compensated following said joining by impregnation with a liquid electrolyte.

46. Process of assembling an electrochemical generator according to claim 27, by joining by lamination or pressing a porous cathodic electrode and an anodic sub-assembly manufactured according to claims 35, 36, 39, 40 and 42.

47. Process of assembling an electrochemical generator according 27, by joining by lamination or pressing two sub-assemblies, one anodic and one cathodic, manufactured according to claims 35, 36, 39 and 42 between which is inserted during said joining a polyether based electrolytic separator less than 10 μm thick containing a solid filler.